Orbital Control in the Dimerization of Polycyclic Aromatic Ketones and Quinones in the Presence of Alkali Metal Alcoholates

Valery F. Traven, Andrew I. Safronov,* Olga F. Shishko and Tatyana A. Chibisova

General-Technical Department, D. I. Mendeleev Russian Chemico-Technological University, 125820 Moscow, Russian Federation. Fax: +7 095 200 4204

Polycyclic aromatic ketones and quinones undergo dimerization in the presence of alkali metal alcoholates; anion-radicals of the substrates are formed under these conditions, and the direction of dimerization depends on the spin density in the intermediate anion-radical.

The carbonyl group allows organic molecules to interact with bases in at least two directions: addition of nucleophile to the carbonyl carbon and reaction as a C–H acid (for compounds with an H-atom at the α-carbon).[1] But there is also a third possibility of engaging in electron transfer. In this reaction ketones and quinones form anion-radicals, particles with an uncoupled electron.[2,3] These particles can take part in certain reactions connected with electron spin density distribution. It is noteworthy to study the reactivity of compounds in which the carbonyl group is connected with a large π-system. We have therefore studied transformations of some polycyclic aromatic ketones and quinones **1–5** in the presence of alkali metal alcoholates, because the formation of various anion-radicals under these conditions is possible.

1,4-Naphthoquinone **1**, phenalenone **2** and benzanthrone **3** are known to undergo dimerization in the presence of alkali metal alcoholates. Dimerization of benzanthrone to 4,4′-dibenzanthronyl has been used in the industrial synthesis of some important vat dyes.[4] However, there are no data concerning the mechanism of dimerization: both carbanions[5] and ion-radicals[6] are suggested as intermediates in this process.

We have found that benzanthrone forms its stable anion-radical on treatment of **3** by alkali metal alcoholates.† We consider this anion-radical to be an intermediate in subsequent dimerization.

According to EPR spectroscopy and quantum chemical calculations (semiempirical method INDO UHF), the maximum value of the spin density is located on the *C*(4) atom of benzanthrone (numbers of the atoms are shown on the structural formulae, calculated spin densities are given in brackets). Experimental and simulated EPR spectra of anion-radical **3** are shown on Fig. 1.

The assumption that anion-radical **3** dimerizes agrees with the concept of frontier orbitals: if the mixing frontier orbitals of reagents have equal energies, the reaction path depends on the maximum value of the eigencoefficients on these frontier orbitals.[7] Therefore, the LUMO of starting molecules **3** determines the direction of dimerization. We confirmed this conclusion by cyclic voltamperometry. Experimental and calculated constants of dimerization are given in Table 1. According to these values the dimerization must take place at position 4 on **3**. The supposition that the anion-radical of **3** is

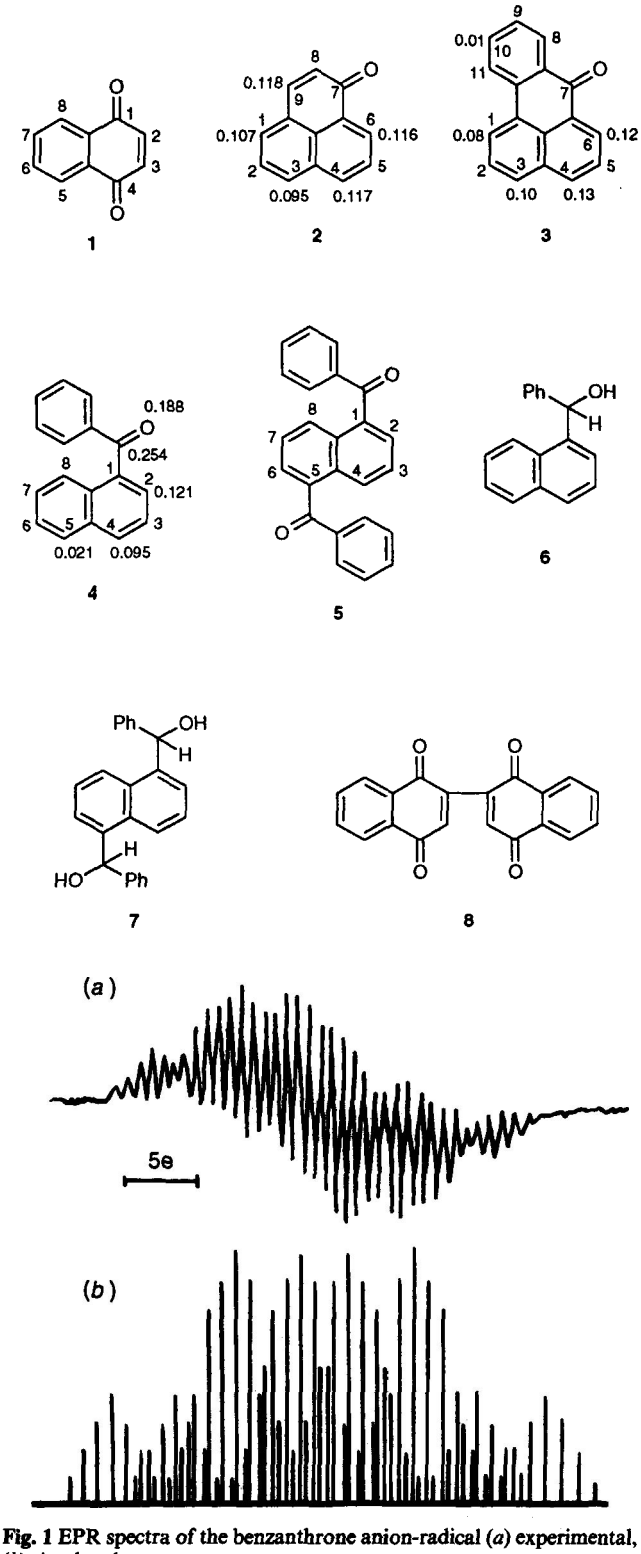

Fig. 1 EPR spectra of the benzanthrone anion-radical (*a*) experimental, (*b*) simulated.

† *Dimerization of benzanthrone.* Benzanthrone (3 g, 0.0129 mol) was added to a solution of KOH (4.2 g, 0.075 mol) in Bu^{t}OH (15 ml) at 90 °C. The mixture was heated with stirring during 2 h at 110 °C and poured into water. The resulting precipitate was filtered, dried and chromatographed on silica gel (40/100μ) with chloroform and the fraction with R_f = 0.37 was separated. 4,4′-Dibenzanthronyl (1 g, 66%) was obtained, m.p. 326–327 °C (lit., 325 °C); *m*/*z* Calc. for $C_{34}H_{20}O_2$ 458. Found, 458.

Transformations of 1-benzoylnaphthalene and 1,5-dibenzoylnaphthalene. 1-Benzoylnaphthalene (1 g, 0.0043 mol) was added to a solution of metallic potassium (1 g, 0.0256 mol) in Bu^{t}OH (15 ml). The mixture was heated with stirring during 3 h at 140–145 °C and was then diluted with water (30 ml) and extracted with benzene. After evaporation, (1-α-hydroxybenzyl)naphthalene (0.82 g, 81.3%) was obtained, m.p. 86 °C (lit.,[15] 88 °C); *m*/*z* Calc. for $C_{17}H_{14}O$, 268. Found, 268.

By analogy, 1,5-bis(α-hydroxybenzyl)naphthalene (0.86 g, 85%) m.p. 168–170 °C was obtained from 1,5-dibenzoylnaphthalene, (1 g, 0.003 mol); *m*/*z* Calc. for $C_{24}H_{20}O_2$, 340. Found, 340; IR (KBr), ν_{max} cm^{-1} 3320 (br), O–H; 1660–1600, 1500–1480, aromatic C=C.

Table 1 Experimental and calculated dimerization constants (in dm^3 mol^{-1} s^{-1}).

Experimental values	Calculated values	
2.71±0.21	2.70[a]	1.42[b]

[a] Values of dimerization for atom in position 4. [b] Values for dimerization for carbonyl group carbon atom.

located on the main path of the reaction coordinate is confirmed by addition of tetracyanoethylene (an electron trap) in the reactions. It can oxidise the anion-radicals to the starting molecule.[8] On addition of tetracyanoethylene the yield of 4,4′-dibenzanthronyl decreased, but no other products were obtained.

1-Benzoylnaphthalene **4** and 1,5-dibenzoylnaphthalene **5** are acyclic analogues of benzanthrone. They gave badly-resolved EPR spectra of the anion-radicals under our conditions. According to EPR spectra and quantum chemical calculations the maximum values of spin density in anion-radicals of **4** and **5** are located on the carbon atoms of the carbonyl groups. Therefore, **4** and **5** undergo reduction of the carbonyl groups under the same conditions and 1-(α-hydroxybenzyl)naphthalene **6** and 1,5-bis(α-hydroxybenzyl)naphthalenes **7** are the main products in reactions with alkali metal alcoholates.

The formation of anion-radicals **1** and **2** has already been reported,[9,10] and we also recorded EPR spectra of **2**. According to this spectrum and INDO UHF calculations, several positions in **2** have high spin density values; for this reason, the direction of dimerization is not so obvious.[11,12] The formation of cross-dimerization products at positions 4 and 7 is reported. Peropyrene derivatives were also obtained in an electrochemical experiment.[13]

The dimerization of polycyclic aromatic quinones follows the same path as aromatic ketones. The structure of the product, 2,2′-dinaphthyl-1,4:1′,4′-diquinone **8**, is in accordance with maximum spin density at position 2(3) of the intermediate anion-radical of starting 1,4-naphthoquinone.[14,‡]

‡ *Dimerization of* 1,4-*naphthoquinone*. Pr^iONa (0.3 g, 0.003 mol) was added to a solution of 1,4-naphthoquinone (0.5 g, 0.003 mol) in Pr^iOH (40 ml) at 50 °C. The mixture was stirred at this temperature during 2 h, then cooled to 20 °C and poured into water (100 ml) with some HCl. The resulting precipitate was chromatographed on silica gel (40/100μ) with benzene–acetone (10:1). The fraction with $R_f = 0.72$ was separated. 2,2′-Binaphthyl-1,4:1′,4′-diquinone was obtained, m.p. 270–271 °C (lit.,[14] 270–271 °C).

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